Self-organization of planar microlenses by periodic precipitation

Christopher J. Campbell, Eric Baker, Marcin Fialkowski, Agnieszka Bitner, Stoyan K. Smoukov, and Bartosz A. Grzybowski

Department of Chemical and Biological Engineering and The Northwestern Institute for Complex Systems, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

(Received 9 December 2004; accepted 10 March 2005; published online 20 June 2005)

Arrays of planar, Fresnel-like microlenses are prepared by a spontaneous chemical process of periodic precipitation (PP) occurring in a thin layer of a dry gel, and initiated by wet stamping. The PP lenses focus white light more efficiently than the conventional Fresnel zone plates of similar dimensions. Nanoscale topographies of the micropatterned gels can be replicated into transparent elastomers, and used for focusing based on optical path differences. Experimental observations for both types of structures are in agreement with the Fresnel diffraction calculations. © 2005 American Institute of Physics. [DOI: 10.1063/1.1899757]

Fresnel zone plates and lenses—that is, optical elements that focus light by diffraction—have important technological applications in x-ray and neutron optics, microwave focusing, and imaging systems. Although current manufacturing methods are capable of high-resolution fabrication of lens arrays, they are limited to binary topographies and/or require expensive and elaborate manufacturing processes. We have previously suggested that self-organization based on reaction-diffusion (RD) can provide a facile and general route to the fabrication of microstructures and microdevices, including optical elements. In particular, using the wet stamping technique (WETS) we developed, we were able to control RD processes in small, complex geometries to prepare microfluidic circuits, and arrays of curved lenses. Here, we use WETS to guide self-organization of arrays of planar microlenses whose optical characteristics are comparable to or better than those of the Fresnel zone plates (FZPs) of similar dimensions. In our system, lenses are created by periodic precipitation induced from ring-shaped sources of silver nitrate on thin layers of dry gels doped with potassium dichromate. The precipitation zones (Lieszegang rings) form optically opaque concentric rings whose spacing and dimensions can be controlled by the concentrations of the chemicals used. In addition, periodic precipitation causes buckling of the patterned substrates; these surface topographies can be replicated into optically transparent elastomers to give quasi-three-dimensional focusing elements with potential applications in microfluidics and waveguides.

Figure 1(a) illustrates the experimental procedure. A 10% w/w high-strength agarose (Omnipur high gel strength agarose, EM Sciences, Darmstadt, Germany) stamp patterned with outlines of lenses (diameter, D = 500–1000 µm) was soaked in an aqueous solution of silver nitrate (AgNO₃, 5%–15% w/w) for 12 h. Gelatin (20% w/w) was doped with potassium dichromate (K₂Cr₂O₇, 0.2% w/w) was first spin-coated on a glass slide at 320 rpm and then dried for 12 h to give a ~10-µm-thick film. The stamp was blotted and blown dry with nitrogen, and then gently applied onto the gelatin. Silver nitrate was transported into the dry film by diffusion enhanced by a gradient of osmotic pressure, and reacted with K₂Cr₂O₇ contained therein. Directly under the stamp, this reaction produced a uniform layer of Ag₂Cr₂O₇; inside the circles, the inwardly diffusing AgNO₃ precipitated periodically with outlines of lenses.

FIG. 1. (Color online) (a) The experimental scheme showing a stamp with outlines of the lenses (D = 500–1000 µm) applied onto a 10-µm gelatin layer doped with K₂Cr₂O₇. The arrows indicate the directions of the diffusion of Ag⁺ cations (black arrows) towards the centers of the circles and of chromate ions (gray arrows) in the opposite direction. Reaction between Ag⁺ and Cr₂O₇²⁻ gives rise to discrete bands of periodic precipitation (bottom graph). The thickness of the bands decreases with the distance r from the middle of the stamped circles (from ~50 µm near the center down to several micrometers near the edge). At the locations of the bands, gelatin buckles up to heights h = 300–1000 nm (insert). (b) The semilogarithmic plot of the position r of the nth precipitation band. (○) D = 500 µm, (■) D = 750 µm, and (△) D = 1000 µm. The data is compiled from periodic precipitation (PP) lenses stamped from 10% w/w AgNO₃. The standard deviations of the ring positions were less than 5% for D = 500 µm, less than 3% for D = 750 µm, and less than 1% for D = 1000 µm. The optical micrographs of the (c) hexagonal (D = 600 µm) and (d) square (D = 500 µm) arrays of lenses with the experimental images of the corresponding focal planes shown in the inserts. The pattern in C is before and that in D is after blackening with formaldehyde. All scale bars are 500 µm.
cally in the form of concentric circles\textsuperscript{14} that served as the basis of the planar lenses. After the reactions were complete, the regions containing Ag\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} were further blackened by the exposure to the vapors of formaldehyde, which reduced the silver salts to black colloidal silver. Buckled topographies of the patterned surfaces were replicated into a transparent elastomer, poly(dimethyl siloxane) (PDMS), by casting its prepolymer against the patterned gelatin and curing overnight at 30 °C.

The radii, \( r_n \), of the periodic precipitation (PP) bands within each circle were well approximated\textsuperscript{19} by the so-called Jablczynski-like law,\textsuperscript{20} \( \ln (R - r_n) \approx (N - n) \), where \( R \) is the lens radius, \( N \) is the total number of resolved bands, \( r_n \) is measured from the circle’s center and \( n \) is the ring number counted from the center outwards [Fig. 1(b)]. In addition, the location of the first distinct band that was resolved near the edge of the circle (i.e., \( n = N \)) depended on the concentration of AgNO\textsubscript{3}; for low concentrations, it was close to the edge of the stamped circle, for high concentrations, it was located further inwards, and the region near the edge was covered by a uniform precipitate (transient precipitation zone).\textsuperscript{21} In all cases, the number of the resolved bands depended on both [AgNO\textsubscript{3}] and the dimensions of the stamped circle, and could be controlled by the amount of time that the stamp was in contact with the gel (the longer the time, the more bands were resolved). The maximum number of bands we obtained was 18 for a 1-mm circle.

The developed PP patterns focused visible light efficiently. This is illustrated in Fig. 1(d), which shows a square array of PP lenses (\( D = 500 \mu m \)) and the corresponding image of the focal plane located \( \sim 4 \) mm away from the plane of the patterned film, and with the focal points \( \sim 15 \mu m \) in diameter.

To determine the focusing ability of our microlenses, we calculated the Fresnel complex-amplitude distribution,\textsuperscript{1} \( U(x) = \int_0^\infty \pi(x_0) \exp(-i2\pi(x-x_0)^2/\lambda dx_0 \) in the plane parallel to that of the patterned film, and located at a distance \( z \) away from it (a “screen”). In the expression above, \( x_0 \) designates the coordinate in the plane of the lens, \( x_s \) is the coordinate along the screen, and \( \lambda \) is the wavelength of light. The transmission function \( \pi(x_s) \) was taken as binary from a digitized optical micrograph of the PP pattern: \( \pi(x_s) = 1 \) for dark precipitation bands and zero otherwise. The intensity of light at the screen was then evaluated by numerical integration as \( I(x_s) = |U(x_s)|^2 \), and the focal distance for a given lens was found by varying \( z \) and finding the minimal value of the width at half height (WHH) of the main intensity peak (zeroth order).\textsuperscript{22} These calculations, performed for a wavelength of light \( \lambda = 532 \) nm, predicted the value of WHH \( \sim 10 \mu m \), in good agreement with the experiment.

Interestingly, modeling indicates that PP lenses have better focusing properties than Fresnel zone plates of similar number of bands. The graphs in Figs. 2(b) and 2(c) compare the intensity profiles in the focal plane of various PP lenses consisting of 17 bands with those of FZPs “designed” to have the same focal distances. In all cases, FZPs must have significantly larger number of bands (40–70) to achieve the same half height width at the focal point. In other words, the FZPs must be larger than PP lenses of identical focusing properties.

In addition to providing an optical contrast between the opaque precipitation zones and the remaining portions of the patterned gel, PP led to the formation of regular arrays of surface microbuckles in the regions corresponding to the precipitation bands. We have previously shown that this effect is due to the Ag\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} collected in the PP bands causing surface deformation that is proportional to its amount at a given location.\textsuperscript{14,23} In the context of the present work, we were interested in replicating the PP surface buckles into optically transparent polymers and investigating the diffractive properties of such materials. Unlike micropatterned elastomers of binary topographies that have been previously used in wave front engineering,\textsuperscript{15,24} our microbuckled surfaces had grooves not only of varying periodicity but also of varying depths (Fig. 3).

The PDMS replicas of the PP patterns proved to be efficient lensing elements focusing light to spots of \( \sim 30–50 \mu m \) in diameter. We note that focusing was not due to the overall residual curvature of the patterns (most notable in those obtained using 5% AgNO\textsubscript{3} solutions). This curvature alone would give a focal point \( z \sim 0.15 \) m away from the lens, based on \( n_{PDMS} = 1.43 \).\textsuperscript{15} In contrast, focal points produced by diffraction were located at \( z \sim 1–2 \) mm. We also briefly mention that the fact that the grooves in the PDMS lenses differed in height improved their focusing...
characteristics—a hypothetical PDMS structure in which the ridges would be located at the same locations, but would have uniform depths would give a much worse focusing. Finally, the PDMS replicas of the PP patterns focused better than PDMS FZPs having the same number of uniform-depth grooves [Fig. 3(c)]

To model light focusing by the PDMS lenses, we accounted for the dependence of the phase function on the optical path through the elastomer. The intensity at a given screen position is given by the equation:

$$I(x_o) = \frac{1}{\pi} \int_{-\infty}^{\infty} I(x) \exp(-i \phi(x)) dx,$$

where $\phi(x) = \frac{2\pi n_{PMDS} - n_{air}}{\lambda} h(x)/\lambda$ is the phase shift due to the lens, $h(x)$ is the height of the lens, $n_{air}$ is the index of refraction in air (1.0), and $n_{PMDS}$ is the index of refraction in PDMS (1.43). The intensities of light at various screen positions were calculated as for the planar PP lenses [Fig. 3(b)], and the results of these calculations were in agreement with what was obtained experimentally [Fig. 3(c)].

In summary, we have described an experimental system in which a spontaneous chemical process initiated from well-defined geometries can produce high-quality optical micro-lenses. The periodic precipitation phenomena we used here can provide a general basis for the fabrication of microstructures and microcomponents of arbitrary shapes. The degree of control over the vertical surface buckling (to within ~50 nm) makes this approach an interesting route to nanostructured surfaces of nonbinary topographies.

One of the authors (B.G.) gratefully acknowledges the financial support from the Northwestern University start-up funds and from the Camille and Henry Dreyfus New Faculty Awards Program. One of the authors (C.C.) was supported in part by the NSF-IGERT program “Dynamics of Complex Systems in Science and Engineering” Grant No. (DGE-9987577).

---

19. The nonlinear correction to the purely linear Jablonskis dependence was due in part to the finite amount of the inner electrolyte inside the circle and in part due to the curvature of the source. These effects will be discussed in detail in an upcoming communication.
21. Formation of periodic precipitation bands requires purely diffusive transport of participating chemicals, and is suppressed by hydrodynamic effects in the vicinity of the source of the outer electrolyte (here, AgNO3). The higher the concentration of this electrolyte, the larger the difference in osmotic pressures between the stamp and the gelatin film, and the larger the transient precipitation zone over which the hydrodynamic effects settle down (cf. Ref. 14).
22. Fresnel lenses have many focal distances (see Ref. 1), but only the farthest focal distance has the greatest intensity. This focal distance was chosen for all of our calculations.
25. As the PDMS is transparent, it was difficult to provide an exact measurement of the experimental focal point.